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### ION EXCHANGE RESEARCH AT CANMET

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July 1991

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Project: 30.52.10  
Solution Purification Development

MINERAL SCIENCES LABORATORIES  
DIVISION REPORT MSL 91-64 (LS)

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32 pp

## **ION EXCHANGE RESEARCH AT CANMET**

by

**David W. Koren**

### **INTRODUCTION**

The purpose of this report is to provide a summary of CANMET publications that have dealt with solution purification by ion exchange. This includes literature surveys and reports on research carried out by CANMET as well as contracted work. The period of time covered is 1960-1990. During this time CANMET's interests could be divided into three categories:

- (1) primary metal recovery (e.g. uranium, gold)
- (2) treatment of mining and milling effluents (e.g. removal of cyanide, etc.)
- (3) development of ion exchange reactors (e.g. fluidized beds)

A brief summary of each category follows; in addition, the abstract or summary of each report which is cited, is provided in the Appendix.

#### **Primary Metal Recovery**

A review of ion exchange extraction systems for solution purification was given by Ritcey (1). The report discusses resins, equipment, processing costs and some specific systems. The fouling of resins by silica which is a common problem encountered in the recovery of metals is discussed in another report (2). Various examples, mechanisms and possible treatments are reviewed.

Most of the work carried out at CANMET on metal recovery has dealt with uranium and gold. A technical and economic evaluation shows ion exchange to be the most favourable process for in situ uranium recovery from underground bio-leach solutions (3). The problems caused by interfering or "poisoning" anions such as tetrathionate, nitrate, chloride and silica

(4,5) as well as methods for the rejuvenation of the resins were investigated (6,7,8). Ion exchange resins were used for the recovery of gold from thiourea (9) and cyanide liquors (10,11,12). For certain ore types, ion exchange was shown to provide a viable alternative to conventional gold recovery processes. A resin which is selective for copper and nickel over iron was also studied (13). Recent work at CANMET has involved the recovery of gallium from Bayer Liquors (14).

### **Treatment of Mining and Milling Effluent**

The introduction of stringent guidelines for effluent streams have forced the mining and milling industry to reduce the levels of pollutants in their waste streams. Since ion exchange can recover materials at low concentrations, a great deal of research involving effluent treatment has been performed.

A literature review of cyanide recovery processes was provided by Gilmore and Gow (15). The feasibility of removing cyanide by ion exchange as an alternative to current practice was studied extensively at CANMET (16-19). This process has the advantage of removing and conserving the cyanide and metals for subsequent recovery. Other processes which also reduced cyanide levels in solutions were compared to the ion exchange process (20,21); it was found that the resin process was the most attractive economically.

Metals such as copper, zinc and nickel were removed from acid-sulphate and alkaline-cyanide waste water using ion exchange resins (22-24). Chloride raffinates were also treated by ion exchange for recovery of zinc, cadmium, copper and lead (25-30). A literature review shows that ion exchange processing would be useful as a scavenging operation to recover cesium (31). Radium removal from chloride liquors to produce environmentally acceptable effluents was performed successfully (32-35). Sulphate, nitrate and chloride ions have also been recovered by the use of ion exchange resins (36-38).

## Development of Ion Exchange Reactors

Considerable progress has been made in the development of continuous ion exchange systems in the past few decades (39). At CANMET, ion exchange recovery of uranium has been carried out with various continuous fluidized bed reactors (40-42). A single stage deep fluidized bed ion exchange column coupled with moving bed elution and wash columns has been developed (43-47). These columns were used for the recovery of gold (48,49) as well as for the processing of a waste stream containing copper (50).

In attempts to reduce costly liquid-solid separation processes, ion exchange techniques have been modified so that unclarified feed solutions could be treated, this is known as Resin-in-Pulp (RIP) processing; Gilmore (51) discussed some of the equipment that could be used to contact resins with leach pulps. The economics of a RIP process have been investigated by Ritcey, Slater and Lucas (52). In this study parameters are defined for the operation and design of a continuous ion exchange process utilizing slurries. A study of the physical stability of several resins for their possible use in RIP processes was also carried out (53); the report emphasizes the importance of selecting a resin with low attrition losses and high metal capacity. Recovery of uranium (41) and gold (49,54,55) has been demonstrated using unclarified feed solutions in a fluidized bed reactor.

**APPENDIX**

- (1) Ritcey, G.M. "Solution purification by ion exchange or solvent extraction" CANMET Report I.C. 237 (1971).

The subject of solution purification using ion exchange or solvent extraction as techniques in hydrometallurgical processing is described. No attempt has been made to cover the many theoretical aspects, but rather to provide an adequate background of information and references useful to those contemplating industrial processing. Among those items covered are the techniques, reagents, equipment, processing costs and selected extraction systems.

- (2) Ritcey, G.M. "Silica fouling in ion exchange, carbon-in-pulp and solvent extraction" CANMET Report MRP/ERP/MSL 85-47 (OP&J) (1985).

Purification of solutions for recovery of metal values can be accomplished by several techniques. Three commonly used processes are solvent extraction, ion exchange and carbon adsorption. However, common to these techniques for purification and metals recovery is the problem of silica in the feed solution. Silica fouling of the three processes occur due to the formation of polymeric species of silica in solution. These polymers cause stable emulsions in solvent extraction circuits and the sorption and blocking of pores in ion exchange resins and in activated carbon. Various examples of silica fouling and the mechanism, and the subsequent treatments necessary for maintaining efficient operation are described in this review of the problem.

- (3) Melis Consulting Engineers, Beak Consultants and Kilborn Ltd. "Technical and economic comparison of uranium recovery from bio-leach solutions by the use of biomass, ion exchange and reverse osmosis" CANMET Contract Report OSQ 85-00159 (1986).

The Biotechnology Section of CANMET, Department of Energy, Mines and Resources, commissioned Melis Consulting Engineers Ltd. to evaluate the technical and economic feasibility of upgrading dilute bioleach solutions from underground leaching of uranium ores by the use of three alternative processes comprising ion exchange,

biomass adsorption and reverse osmosis. This study was accomplished in association with Beak Consultants Limited, who were responsible for the literature review component of the study, and Kilborn Ltd., who assisted with the capital cost estimate of the three options evaluated.

- (4) Gilmore, A.J. "Some competing and poisoning anions encountered in the anion exchange recovery of uranium" CANMET Report ERP/MSL 78-152 (LS) (1978).

Flood leaching of ore piles may prevent tetrathionate formation in dump or heap leaching of low-grade uranium ores containing pyrite, i.e., by the construction of 2 ft berms around the top of ore dumps to hold an 18 inch depth of recycled leachate. The purpose is to prevent, as much as possible, wet and drying zones in the ore pile as proposed by a CANMET investigator. This same research reports that tetrathionate poisoning of resin is minimized when leachate contains  $< 3\text{ppm Na}_2\text{S}_4\text{O}_6$ .

A slightly alkaline cyanidation waste successfully removed polythionates and silica from strong base resins at Stilfontein in South Africa. Caustic (NaOH) is most commonly used to remove the polythionates and silica resin contaminants. The caustic reagent unfortunately, has escalated to about 0.16 \$/lb and has become a noticeable operating expenditure. Milder alkaline reagents, such as  $\text{Na}_2\text{CO}_3$  at 0.05 \$/lb or milk of lime at 0.016 \$/lb may be as effective as the caustic with a potential saving in operating cost. Operational uranium mills in South Africa have had to rejuvenate their resin at intervals of from 1 to 12 times a year. The milder reagents may also reduce the osmotic shock that the resin is subjected to in rapid changes from one resin form to another with relatively strong reagents such as NaOH and  $\text{H}_2\text{SO}_4$ . Rupture of the resin may occur by too great a shock or change to the resin structure.

The introduction of nitrate and chloride anions into Ion-exchange influent, by recycling the Royal Barren may be controlled by using the minimum concentrations of nitrate and chloride reagents for efficient uranium desorption. Another method is to perform a precipitation recovery of the uranium in the Royal Barren, then recycle the uranium precipitate to the leach circuit and discharge tolerable concentrations of the filtrate with dilution.

Nitrate, originating from explosives, may be minimized or eliminated by (1) maintaining rigid housekeeping of explosives underground and (2) a spray wash of the blasted ore in the stopes with clean, hot water at 60 to 70°C. A 3-stage recycle wash of the blasted ore would minimize water volumes.

- (5) Gilmore, A.J. "The behaviour of some anions during the ion exchange recovery of uranium from an acidic bacterial leach liquor" CANMET Report ERP/MSL 79-13 (OP) (1979).

The objective of this work was to study the ion exchange processing of uranium sulphate leach liquors, from an acidic-bacterial operation, containing concentrations of interfering anions such as tetrathionates ( $\text{SO}_4^{2-}$ ), nitrate ( $\text{NO}_3^-$ ), chloride ( $\text{Cl}^-$ ) etc. The study indicated areas where uranium recovery and consequently the economics may be improved. Competing and poisoning anions originating during the  $\text{H}_2\text{SO}_4$  processing of uranium bearing ores, can become a problem affecting the economics of the anion exchange recovery of uranium. Competing anions, such as nitrates and chlorides, contend for resin sites with uranyl-sulphate complex.

Underground blasting with nitrates is considered to be a constant source of the nitrate on coarsely blasted ore. The chloride anion is probably derived from the chlorapatite mineral  $[(\text{CaCl}_2)\text{Ca}_4(\text{PO}_4)_3]$  in the ore being treated. Poisoning anions, such as tetrathionates produced by the atmospheric oxidation of pyrite and other sulphide minerals, can occupy resin sites during the adsorption phase. A number of serious problems, related to ion exchange recovery, may often be eliminated by problem solving at the point in the circuit where the problem originates and before the process liquor reaches the recovery circuit.

- (6) Gilmore, A.J. "Rejuvenation processes applied to poisoned anion exchangers in uranium processing - A review" CANMET Report ERP/MSL 79-148 (LS) (1979).

The removal of poisons from anion exchangers in uranium processing of Canadian radioactive ores is commonly called rejuvenation or regeneration. The economics of the ion exchange recovery of uranium is adversely affected by a decrease in the capacity and efficiency of the anion exchangers, due to being poisoned by silica, elemental sulphur, molybdenum and tetrathionates. These poisons have a high affinity for the anion exchanger, are preferentially adsorbed to the uranyl desorption phase. The frequency of rejuvenation and the reagents required for rejuvenation are determined by the severity of the poisoning accumulated by the exchanger in contact with the uranium leach liquor.

Caustic soda ( $\text{NaOH}$ ), at 0.18\$/lb is commonly used to remove uranium anion exchangers of tetrathionate ( $\text{S}_4\text{O}_6^{2-}$ ) poisons. A potential saving in operating cost would be of consequence if other reagents, e.g., sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) at 0.036 \$/lb or

calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) at 0.019 \$/lb were effective in removing  $\text{S}_4\text{O}_6^{2-}$  from a poisoned exchanger. A rejuvenation process for a test program was adopted after a perusal of the literature.

- (7) Gilmore, A.J. "The rejuvenation of a tetrathionate poisoned anion exchanger in uranium processing" CANMET Report ERP/MSL 80-76 (TR) (1980).

Uranium loadings have shown that  $\text{Na}_2\text{CO}_3$  and  $\text{Ca}(\text{OH})_2$  reagents are as satisfactory as the  $\text{NaOH}$  reagent for the rejuvenation of a tetrathionate poisoned anion exchange, Duolite A-101D.

The experimental results indicate that  $\text{Na}_2\text{CO}_3$  and  $\text{Ca}(\text{OH})_2$  rejuvenation would be less costly than the conventional  $\text{NaOH}$  rejuvenation.

The results indicate that, while not tried experimentally, the recycling of rejuvenation solutions and  $\text{NaCl}$  washes, as discussed in this report, would have the effect of lowering alkali rejuvenation costs still further.

- (8) Gilmore, A.J. "The rejuvenation of a silica poisoned anion exchanger in uranium processing" CANMET Report ERP/MSL 83-105 (TR) (1983).

This investigative study was performed to assess the feasibility and economics of using alkaline reagents, less expensive and costly sodium hydroxide, for the rejuvenation of silica poisoned resins. Anion exchange resins are used in the processing of radioactive ores for the separation and recovery of uranium from leach liquors. Silica poisoned resins, arising from the  $\text{H}_2\text{SO}_4$  leaching of siliceous minerals in the ore, (1) decrease uranium adsorption and desorption efficiencies, and (2), lower exchanger resin capacity for uranium, as illustrated in test results.

An operating mill superintendent can little afford the  $\text{NaOH}$  rejuvenation more than once a year, due to the excessive cost of the  $\text{NaOH}$  reagent. This study concluded that a silica poison removal technique, employing sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) rejuvenation plus a  $\text{NaCl}$  wash, costs only 37% that of the  $\text{NaOH}$  rejuvenation plus the  $\text{NaCl}$  wash. Rejuvenation costs, the study indicates, could be further reduced by recycling some of the rejuvenation and  $\text{NaCl}$  wash solutions. Furthermore, a 13%  $\text{H}_2\text{SO}_4$  uranium desorption displaced 8.6 times more silica than the uranyl sulphate [ $\text{UO}_2(\text{SO}_4)_3^{4-}$ ] adsorption.

- (9) Deschenes, G., Prud'homme, P.J. and Wong, E.W. "Recovery of gold from thiourea solutions: Investigation of cementation with metal powder, activated carbon, ion exchangers and solvent extraction - A progress report" CANMET Report MSL 86-26 (TR) (1986).  
see also Proc. Int. Gold Metall. 1987, 359-377.

This progress report shows the actual results obtained for gold recovery from thiourea solutions. Cementation with aluminum and lead powders, adsorption with activated carbon, ion exchange with strong acid cationic resins and solvent extraction have been studied.

Cementation with alumina powder is efficient and high extraction is provided (98%). However, quality of alumina cement is poor. Cementation with lead powder is totally inefficient. Activated carbon extracts almost all gold (99%) but performance is overshadowed by a high loss of thiourea during carbon loading. Strong acid cationic resins provide high and selective extraction of gold but elution with thiourea has not been successful to date. However, elution of the ion exchanger with a thiosulphate solution was interesting providing 97% gold stripping in preliminary tests. Solvent extraction of gold was selectively realized with a mixture of di-2-ethyl hexyl phosphonic acid and tributyl-phosphate. Stripping of the organic to recover gold is easily achieved in hydrochloric solution with 98% of the gold stripped.

- (10) Muir, D.M. "Prospects for the recovery of gold from cyanide liquors and pulps by solvent extraction and by ion exchange" CANMET Report MSL 88-78 (1988).

A review of current developments in resin and solvent technology as possible alternatives to carbon for recovering gold from cyanide leach slurries has been carried out together with an analysis of the costs associated with gold mining and processing to establish the economic constraints for any new process. Recent studies have shown that currently available commercial resins have attractive physical properties but limited chemical properties and do not compare favourably with carbon economically. New solvent extraction systems, however, particularly quaternary amines like Aliquat 336, offer the prospect of better chemical properties provided solvent losses are not excessive. The quaternary amine system coupled with air-sparged thiourea stripping appears to have merits for applications to clarified leach solutions but the best economic advantage is gained if solvents can be applied to pulps directly.

A survey of previous solvent-in-pulp (S.I.P.) work on uranium leach slurries using a tertiary amine extractant like Alamine 336, identified a number of practical problems and variable solvent losses. Thus a detailed investigation of the various factors involved in S.I.P. has been undertaken with particular regard to understanding the principles and causes of emulsion and crud formation, flocculation, and adsorption of organics on mineral surfaces. Tests have been carried out to determine the best type of flocculant for S.I.P. on a local ore and to establish adsorption isotherms for Aliquat 336 and Alamine 336 on a silicate ore, pure quartz, a pyrite concentrate, and pure pyrite. The effects of particle size, pH, and various inorganic and organic pre-treatment additives were examined to try to minimize amine adsorption. It was found that adsorption of amine onto the pulp also led to adsorption of  $\text{Au}(\text{CN})_2^-$  from the liquor resulting in poor gold recovery. Rates of transfer of Aliquat 336 and  $\text{Au}(\text{CN})_2^-$  between water and the organic phase were found to be comparable and apparently limited by mass transfer across the interface. Moreover, using contactor designs with minimum agitation to prevent dispersion of the organic, rates of  $\text{Au}(\text{CN})_2^-$  extraction were very slow. More consideration of the organic adsorption onto minerals and contactor design is needed before S.I.P. can offer a viable alternative to C.I.P.

- (11) Riveros, P.A. "Advances in ion exchange and solvent extraction for gold recovery" CANMET/OMA Conference Timmins, Ontario, November 22 and 23, 1988.

Recent work on the application of ion exchange and solvent extraction technology to gold recovery from cyanide media is reviewed. Ion exchange is emerging as a viable alternative to conventional gold recovery technology. Solvent extraction shows great promise, especially if present attempts to develop a solvent-in-pulp process are successful.

- (12) Riveros, P.A. "Evaluation of ion exchange resins for the extraction of gold from cyanide leach solutions" CANMET Report MSL 90-5 (CF) (1990). Presented at the Randol Gold Forum '90, Squaw Valley, California, September 13-15, 1990.

Various types of commercial ion exchange resins were evaluated with respect to their ability to extract gold from cyanide leach solutions. Large differences were found among the various resins in terms of selectivity and gold loading. The hydrophilicity and

the charge density appear to be the main factors that determine the resin characteristics. Polystyrene weak-base resins, such as Dowex MWA-1, exhibited the best all around performance.

- (13) Prud'homme, P. "Investigation of new selective ion exchange resins for copper and nickel" CANMET Report MRP/MSL 78-34 (TR) (1978).

Two new chelating ion exchange resins, XF-4195 and XF-4196, developed by Dow Chemical, have been tested in the CANMET laboratory to study their selectivity performance to absorb copper and nickel in preference to ferric iron at pH 2 from synthetic copper sulphate leach solutions.

Elution tests have also been carried out to find a proper eluant solution for each of these resins which would give the best desorption efficiency. Densities of loaded and unloaded resins have also been determined for each.

Both resins exhibited high selectivity and capacity for copper absorption compared to ferric iron and other metal cations such as nickel, aluminum and magnesium present in low pH sulphuric acid solutions. The adsorbed copper and nickel can be readily stripped from both resins using a 1N ammonium hydroxide solution. If sulphuric acid is used, a 2N  $H_2SO_4$  solution is necessary to achieve an effective elution of resin XF-4196 while a 10N  $H_2SO_4$  solution is necessary for resin XF-4195. Loaded resin densities of 1.1995 and 1.204 respectively were determined for resins XF-4195 and XF-4196.

- (14) Riveros, P.A. "Recovery of gallium from Bayer liquors with an amidoxime resin" Hydrometallurgy 25 (1990) 1-18.

The extraction of gallium from Bayer solutions with the commercial amidoxime resin Duolite ES-346 was studied. While the loading, selectivity and kinetics are quite favourable, the long term performance of the resin hinges on the degradation of the amidoxime groups in acid media and by the build-up of vanadium. Possible ways to circumvent these problems are discussed.

- (15) Gilmore, A.J. and Gow, W.A. "Cyanide recovery from gold-barren waste solutions: A literature review" CANMET Report I.C. 145 (1963).

The literature has been reviewed to assess the possibilities of economically recovering cyanide from alkaline waste solutions from Canadian gold-milling operations.

The literature cites two possible processes. In one process the alkaline waste solution is acidified with sulphuric acid to convert the free and combined cyanide to hydrocyanic acid, which is absorbed in a lime slurry. The other process was developed to the pilot plant stage in South Africa. It involves an ion exchange technique. By use of both anion and cation exchangers, both the cyanide and the base metals, present as metal cyanide complexes, are recovered.

Cyanide recovery by these two processes were uneconomic at the time this report was written but new environmental guidelines may make them economically feasible today.

- (16) Gilmore, A.J. "Cyanide removal from cyanidation wastes for environmental benefit - by ion exchange technology" CANMET Report ERP/MSL 75-122 (TR) (1975).

The objective of the work described here is to investigate the feasibility of removing cyanide and toxic heavy metal cyanide complexes, using ion exchange technology, from cyanidation wastes for the preservation of fish and other aquatic life in our Canadian natural waters. Environment Canada, under the authority of the Fisheries Act, has been charged to establish environmental guidelines for cyanide emanating from gold milling operations in cyanidation effluent wastes. The tentative objective is 0.1 ppm total cyanide (CN(t)) in these effluents to our water environment.

The feasibility of removing toxic cyanides to 0.1 ppm CN(t) is being studied in our laboratory using, basically, the Stilfontein ion-exchange process, as piloted by Goldblatt. This process, performed as a CANMET joint project with some Canadian gold producers, has the virtue of removing and conserving the cyanide and metals for recycling. Process effluents, devoid of toxic concentrations of both cyanide and metals, could be discharged to the natural water courses or recycled to the mill operation.

- (17) Gilmore, A.J. "The removal of cyanide and metal-cyanide complexes from cyanidation wastes by fixed bed ion exchange technology" CANMET Report MRP/MSL (CF) 76-19 (IR) (1976).

The objective of this investigation was to study the technical feasibility of removing toxic cyanide from six cyanidation wastes by static bed ion exchange

technology. The removal of cyanide would preserve fish life in our Canadian natural waters. Otherwise, the fish life would be endangered by these toxic free cyanide and heavy metal complex cyanides in the discharged waste. Environment Canada set a tentative environmental objective of 0.1 ppm total cyanide (CN(t)) emanating from "end of the pipe" effluents from gold mill operations.

The study, on the six cyanidation wastes, has demonstrated the technical feasibility of;

- (1) achieving the environmental objective of  $<0.1$  ppm total cyanide,
- (2) the removal of the heavy metals to the range of  $<10$  to  $70$  ppb for each of Cu, Ni and Zn,
- (3) the removal of thiocyanate to  $<1$  ppm CNS,
- (4) a 1%  $H_2SO_4$  desorption and recovery of the cyanide as HCN in a caustic media,
- (5) obtaining resin loadings equivalent to 2 to 4 lb CN/cu. ft. resin,
- (6) the recovery of bulk products of the heavy metals equivalent to 98.9%  $ZnO + CuO + NiO$ ,
- (7) a water wash of the resin columns, after the acid desorption of HCN, converted the primary column to  $SO_4^-$  form for next adsorption and recovered 6 to 15% of  $H_2SO_4$ . This acidic wash could be (a) reconstituted to 1%  $H_2SO_4$  for a subsequent cyanide desorption, or (b) used to acidify brine regenerant for desorption and recovery of the heavy metals from the cation exchanger.

- (18) Gilmore, A.J. "The ion exchange removal of cyanide from gold mill wastes for environmental benefit" CANMET Report MRP/MSL (CF) 76-26 (IR) (1976).

The study has demonstrated the chemical feasibility of adsorbing free cyanide and heavy metal cyanide complexes on  $SO_4^{2-}$  form anion exchanger in fixed beds,

- (1) almost 3000 bed volumes of the cyanidation waste were put through 150 mL resin beds of Amberlite IRA-400 before CN(t) breakthrough at 0.1 ppm.
- (2) cyanide loadings of up to almost 3 lb CN/cu ft resin were obtained.
- (3) flowrates of up to 6.54 L/h or the equivalent of 4.53 gallons/min/cu ft through the 150 mL columns were achieved, to produce an effluent of  $<0.1$  ppm CN.
- (4) the investigation was terminated due to financial and time limitations.
- (5) capital and operating costs, based on the limited amount of work accomplished, were estimated at 1.34 \$/lb NaCN recovered.

- (19) Ritcey, G.M. "Treatment of gold mill effluents for removal and recovery or destruction of cyanide - A summary of the joint project with six gold mills" CANMET Report MRP/MSL (CF) 77-15 (IR) (1977).

This report is a summary of a program undertaken by CANMET, in co-operation with six producing gold mills, on the treatment of effluents for the removal of cyanide. The object was to examine different process routes and determine the best practical technology for achieving 0.1 ppm total CN in the effluent. The routes that were examined in the laboratory and in the small continuous pilot plant operations, were acidification-volatilization-reneutralization, ion exchange and alkali chlorination. The report describes the summarized data obtained in those investigations, together with the results of work by other investigators on the use of ozonation.

Comparative estimates, based on an effluent containing 40 ppm total cyanide at a flow rate of 125 gal/min, are shown for each of the processes. The data indicate the alkali-chlorination or ozonation processes to be the most economical routes. Although the ozonation required higher capital expense compared to the alkali-chlorination, the operating costs were higher in the latter route, resulting in a slight advantage for the ozonation process. Cost estimates are also given for these two processes, based on the effluents for each of the six gold mills. Also included are the major advantages and disadvantages and flowsheets of each of the four routes. Naturally, with each mill differing in solution feed and in their individual plant designs and bleed streams, the route ultimately selected would have to suit the particular requirements of that mill.

- (20) Ritcey, G.M. "Treatment of gold mill tailings" CANMET Report MRP/MSL 85-51 (OP) (1985).

There are many available methods for the treatment of cyanide solutions arising from gold mill operations for the destruction or the recovery of cyanide. Each have certain features and therefore in comparison of the advantages and disadvantages, the solution feed type and composition must also be compared.

A comparison of process costs of the 4 routes examined by CANMET are provided. They are based on an effluent stream containing 40 ppm metallic and free cyanides, plus 40 ppm CNS, at a flow rate of 125 gal/min. All routes are based on achieving 0.1 ppm residual cyanide, except for the acidification process which is based on 1.0 ppm. Based on the advantages and disadvantages, the relative costs, and the possibility of recovery

of cyanide and metals, the ion exchange process would appear to be the most attractive for this very dilute barren bleed feedstock. The process schemes would have to be evaluated and compared on the particular feed stream requiring cyanide removal or destruction.

De Gussa Corporation in Germany have also investigated a number of treatment methods for cyanide destruction or removal. A summary of their results indicates that ion exchange has the best promise for success.

- (21) Laird, J.L. and Witte, M.K. Witteck Development Inc. "Gold mill effluent treatment utilizing ion exchange technology - Volumes I and II" CANMET Contract Report 1SQ 85-00163 (1986).

The paper reports on the results of Phase I of a three phase test and feasibility study entitled "Gold Mill Effluent Treatment Utilizing Ion Exchange Technology" (DSS Contract 03SQ.23440-5-9121).

One of the objectives of this study was to survey the gold milling industry to assess the current status of effluent treatment and to determine the need for new technology. The response to the industry survey indicated a larger effluent treatment concern with operations utilizing carbon-in-pulp circuits than with operations which use zinc precipitation circuits. This is due primarily to the latter's ability to recycle zinc precipitation barren within the plant, and therefore having to discharge only a portion from the mill.

Most operations indicated that a significant cost saving could result from the recovery and recycle of cyanide. Any new technology which could incorporate cyanide recycle with effluent treatment might be very attractive economically. This would have to be evaluated in terms of operational cost savings and payback of capital costs.

The results of the current test program on the CANMET two column system for the recovery of both the metal complexed cyanides (column I) and free cyanide (column II) are summarized below:

- Greater than 90% of the cyanide present in the waste effluent solution can be recovered as a concentrated NaCN solution.
- A portion of the column I effluent, which contains only lime, free cyanide and thiocyanate can be used as the alkaline trap for cyanide recovery.
- Acceptable barren effluent is produced by the two column process [ $<0.01$  ppm Cu,  $<0.02$  ppm Fe,  $<0.01$  ppm Ni,  $<0.01$  ppm Zn,  $<0.05$  ppm Co,

<0.05 ppm Pb, <1 ppm SCN, <1 ppm CN(t)]. The 1 ppm target currently recommended by most provincial governments is achieved easily. A more serious effluent problem would be the leakage of arsenic and antimony in the column effluent; neither of which are adsorbed efficiently by the resin. As with the destructive processes, arsenic precipitation using ferric iron would have to be used in conjunction with the ion exchange technology.

- A procedure developed in 1981 by Witteck in collaboration with Lac Minerals Ltd. recovers copper, nickel, zinc and cyanide efficiently from the resin.
- Cyclic testwork on the column I technology indicated no build-up of copper, nickel nor zinc on the resin. However, iron and cobalt were identified as resin poisoning agents.
- A number of loading tests were carried out to find a resin and conditions under which antimony and arsenic could be removed from the effluent using ion exchange technology. Unfortunately, loading efficiencies were poor under a variety of conditions.
- The cuprocyanide form of the resin was compared to the sulphate and hydroxide forms for column II. The sulphate form displayed the lowest loading capacities to breakthrough. The cuprocyanide form displayed higher equilibrium capacity (32 mg CN/mL resin) than did the hydroxide form (25 mg CN/mL resin). However, while the cuprocyanide form did not achieve the target level of 0.1 ppm CN(t) in the column effluent, the hydroxide form did.

(22) Gilmore, A.J. "Ion exchange recovery of copper, zinc and nickel from acid-sulphate and alkaline-cyanide waste water" CANMET Report I.C. 252 (1970).

The literature of the past twenty years describing the use of ion exchange methods for the treatment of copper, zinc and nickel bearing acid sulphate or alkaline-cyanide wastes is reviewed. Application of sulphonic, carboxylic and weak base ion exchange resins to the treatment of a variety of base metal bearing solutions from industrial plants and mines are described. One investigation of the treatment of alkaline cyanide solution containing base-metal-cyanide complexes with a strong base ion exchange resin is reviewed. The literature suggests that an ion exchange process based on a sulphonic type resin could be useful for the treatment of acid-sulphate mine or metallurgical waste, but further work to develop design criteria is necessary. Further work of a more preliminary

nature is needed to determine whether present ion exchange media have a potential application to the treatment of alkaline cyanide waste solutions.

- (23) Gilmore, A.J. "Recovery of copper and zinc from mine waste effluents with carboxylic type ion exchange resins" CANMET Report T.B. 127 (1970).

The recovery of copper and zinc from synthesized mine waste effluents containing up to 7 g/L of total metal with the Rohm and Haas Limited carboxylic type resins Amberlite IRC 50 and IRC 84 has been investigated. The adsorption characteristics of the resins from the  $\text{Na}^+$ ,  $\text{NH}_4^+$ , and  $\text{H}^+$  forms at feed pH values of from 3.6 to 6.0 were determined. The results of the work showed that under all conditions investigated the metals broke through very early in the adsorption cycle. An ion exchange operation run under these conditions to produce an effluent containing  $<0.1$  ppm of metal could be expensive, due to high capital cost in equipment and resin inventory.

- (24) Gilmore, A.J. "A proposed hydrometallurgical process for the separation and recovery of toxic heavy metals - A progress report" CANMET Report MRP/MSL 75-142 (IR) (1975).

The feasibility of (1) separating chloro-complexes of heavy metals from each other in a brine media, then (2) recovering high-grade metal products by neutralization of exchanger effluents, has been demonstrated. This separation technique for heavy-metal chloro-complexes would be of environmental benefit for the recovery of high-grade heavy-metal products from dilute toxic concentrations in acid mine drainage (AMD) waters. The technique, also, has potential in the hydrometallurgical processing of mill leach bearing heavy metals.

The hydrometallurgical separation of metal chloro-complexes, is worthy of consideration along with alternative processes when metal recovery, concentration and separation techniques are being considered.

- (25) Gilmore, A.J. "The removal of metals from chloride raffinates by ion exchange - Interim report no. 1" CANMET Report MRP/MSL 77-337 (TR) (1977).

Under the test conditions, Ionac A-365 was the only resin to produce a bulk removal of the marketable metals from the pH 2.0 - 3M NaCl liquor. The concentration

of metals in the effluents were adequately low for recycling to the process, but they were too high for discharge to the tailings area and the water environment. These effluents would require further treatment, possibly by precipitation, to achieve the stringent water quality criteria before discharge to tailings or the New Brunswick water environment.

The Dowex-1 resin, appeared to be selective to the Zn- and Cd-complexes under test conditions. The Amberlite IRA-93 resin had little merit. It appeared to adsorb all the metals, but had little or no discardable effluent. The Chelex-100 adsorbed most of the metal cations and produced a minimum of effluent with up to 4 ppm of metal. The unadsorbed silver could possibly be scavenged on an activated charcoal column.

- (26) Gilmore, A.J. "The recovery of zinc from a mine water containing small amounts of alkali and heavy metals" CIM Bulletin 1977, 70 (780) 142-146.

A lab study was made of base metal mine water containing Zn 380, Ca 470, Mg 260, Mn 27 and Na 25 ppm at pH 6.5. Clarified mine water was fed through a columnar bed of Na form Amberlite IR-120. The regenerant was 2N NaCl acidified to pH 2.0 with  $H_2SO_4$ , which desorbed the loaded exchanger in 12 bed volumes. Regenerant flows were equivalent to retention times of 6.8-10 min. Zn was precipitated from a high grade fraction of the chloride regenerant by increasing the pH to 7.0 with 5% NaOH solution. The filtered ppt was washed with hot water, then calcined at 200°C to decompose the ppt to a 91.1% ZnO product.

- (27) Gilmore, A.J. "The removal of metals from chloride raffinates by ion exchange - Interim report no. 2" CANMET Report MRP/MSL 78-24 (TR) (1978).

Demineralized water was effective in the metal-complex desorption of the anion exchangers. It was more effective for the strong base Dowex-1 exchanger than for the weak-base exchangers, Ionac A-365 and Amberlite IRA-93. While water is good for zinc and cadmium desorption of anion exchangers, a study of the various concentrations of HCl may be necessary to completely desorb the metal complexes adsorbed on the exchangers used previously.

Further study of the HCl-desorption of the Chelex-100 cation exchanger is also necessary to divest the resin of all the adsorbed cations.

- (28) Gilmore, A.J. "The removal of metals from chloride raffinates by ion exchange - Interim report no. 3" CANMET Report MRP/MSL 78-74 (TR) (1978).

The Amberlite XE-318 chelating resin is the best of the resins tested for the bulk removal of 50% of the transition metal cations under the test conditions, with the influent at pH 4.7 and containing 3M NaCl. The other 50% of the metal cations would have to be removed by an auxilliary absorbent or by precipitation. The effluent would be too high in metal concentration for discharge to the mill tailings or the water environment, but is sufficiently low for recycling to the process.

The volume of influent treated by the Chelex-100 at pH 4.7 was less than for the Amberlite XE-318. The loading of copper on Chelex-100, which is one of the principal metals for recovery, would be minimal in volume. Gold, Ag, Bi and Sb would have to be recovered by an auxilliary adsorber.

The Cl- form Ionac A-365 exchanger does not appear to be practical for the pH 2.0-3M NaCl influent. The barren effluent volume is negligible and consequently the loadings would be very minimal.

- (29) Gilmore, A.J. "The removal of metals from chloride raffinates - Interim report no. 5" CANMET Report MRP/MSL 79-68 (TR) (1979).

The Amberlite XE-318 resin proved to be the best bulk adsorber of the metal cations, with the exception of the Fe, from the 3M NaCl. Ionac A-365 ranked second to the Amberlite XE-318 for the bulk removal of metals. A proposed columnar arrangement for the bulk removal of cations is given.

A series adsorption is suggested for selective separation of the seven metal complexes in the pH 4.0 influent. The first column would be charged with the Dowex 1-X8 to selectively adsorb the Zn and Cd chloro-complexes with respectable loadings. The order of preference for the strong base exchangers in order of anticipated loading is Dowex 1-X8 > Amberlite IRA-400 > Zerolite FF > Duolite A101D = Amberlite IRA-410 > Amberlite IRA-910.

The effluent from the lead column, containing Cu, Pb, Mn, Co and Fe would pass through a second bed of Dowex WGR weak base exchanger to adsorb primarily Pb and Cu. Minor amounts of Co would also be adsorbed but the majority would pass through the Dowex WGR.

The effluent from the third column would pass through an exchanger of Ionac A-365 for adsorption of the Mn. The Fe would pass through in the effluent. The proposed flowsheets would have to be confirmed by continuous operation.

The strong acid exchangers Zerolite-265 and Amberlite IR-120, out of the 14 exchangers tested, did not adsorb any of the available cations from the pH 4.0 3M NaCl solution. This nonadsorption was probably due to interference from the relative large mass of  $\text{Na}^+$  cations present.

A desorption program is necessary to study the displacement of adsorbed metal chloro-complexes from the exchangers discussed.

- (30) Mackinnon, D.J. and Kilpatrick, M.W. "Preliminary studies on the extraction of base metals from chloride solutions using chelating ion exchange resins" CANMET Report MRP/MSL 78-199 (TR) (1978).

Preliminary studies have been completed on the use of Dow Chemical chelating ion exchange resins XF 4195 and XF 4196 for extracting base metals from chloride solutions. Both resins were effective in extracting  $>95\%$   $\text{Cu}^{2+}$  from zinc chloride solutions over the pH range 0.5 to 2.0. Only XF 4196, however, showed good selectivity for  $\text{Cu}^{2+}$  over other base metal ions such as  $\text{Fe}^{3+}$  and  $\text{Zn}^{2+}$ , provided the total chloride ion concentration was  $<1\text{M}$  and the equilibrium pH was about 1.5.

- (31) Gilmore, A.J. "Separation and recovery of cesium carbonate by ion exchange or solvent extraction - A review summary" CANMET Report EMI 74-10 (1974).

This report is a summarized review of literature concerning the separation and recovery of cesium as cesium carbonate by means of ion exchange or solvent extractive processing. The review covers the period 1960-1974, and also included are possible scavenging techniques for treating effluents containing cesium.

- (32) Gilmore, A.J. "The removal of radioactive radium (Ra-226) from chloride leach liquors by ion exchange - Progress report" CANMET Report MRP/MSL 79-154 (TR) (1979).

Radium-226 removal from synthetic chloride liquors has been accomplished by adsorption on Dowex-50 and Ionac NC-11 cation exchangers in the  $\text{H}^+$  form. This technology will ultimately be duplicated on chloride liquors produced by the chloride

leaching of radioactive uranium ores. The isolation of radium-226 is required, as it has been declared a public health hazard due to its gamma radiation. Cancer and infertility are promoted by excessive exposure to these radium radiations.

Dowex-50 and Ionac NC-11 resins, in preliminary work, produced barren effluents of 5 and < 5 pCi Ra/litre from synthetic chloride liquors, containing 2000 and 20,000 pCi Ra/litre at pH 1.4 and 4.0. Ion exchange technology has demonstrated (a) the capability of >99% removal of Ra-226 (b) a concentration reduction of up to 4720/1 and (C) the potential for resource recovery from a minimum concentrated volume should a Ra-226 market develop at a future date. The effect of 120-750 ppm Fe, 10-500 ppm Ca and 5-100 ppm Mg on resin loadings for Ra-226 still has to be studied.

- (33) Gilmore, A.J. "The removal of radioactive radium (Ra-226), in the presence of calcium, magnesium and iron cations from chloride liquors by ion exchange - Progress report no. 2" CANMET Report ERP/MSL 81-2 (1981).

Ra-226 resin loading increases with increasing pH of pure Ra-226 solutions in the pH range 1.3 to 4.0, according to batch adsorption work with sulphonated acid type resins. Resin loading was  $5.5 \times 10^8$  Ra-226/litre resin from a pure solution pH of 1.3, and in excess of  $23.4 \times 10^8$  pCi Ra-226/litre resin from a pure solution pH of 4.0.

The amount of Ra adsorption and loading is dependent on the concentration of other cations, like Ca, Mg and Fe. The concentration of the contaminating cations has a greater effect on Ra loadings than pH. The possibility exists that an ion exchange control system for Ra removal is not feasible due to the serious contamination of a number of cations at various concentrations in the raffinate bleed. A prior precipitation stage to form  $\text{RaBa}(\text{SO}_4)_2$  is suggested. Then dissolved Ra would be adsorbed onto an adsorbent so that Ra and resin could be discarded in a place of a wet voluminous sludge of  $\text{RaBa}(\text{SO}_4)_2$ . In this manner two toxic elements, Ra and Ba would be isolated by disposal instead of just Ra.

- (34) Gilmore, A.J. "The removal of radioactive radium (Ra-226) from chloride liquors by columnar ion exchange in the presence of calcium, magnesium and iron cations - Progress report no. 3" CANMET Report ERP/MSL 81-70 (TR) (1981).

The purpose of this work was to study the feasibility of controlling the discharge of soluble Ra-226, in the presence of Ca, Mg and Fe cations in synthetic chloride

effluents by adsorption on cation resins to decrease Ra concentrations to federal environmental levels of 10 pCi Ra/litre. Environmentally acceptable effluents were produced from synthetic chloride feed liquors containing 10 ppm Ca, 5 ppm Mg, 120 ppm Fe plus 20,000 pCi Ra/litre. Environmentally acceptable effluents were not produced, by cation exchange, from a synthetic chloride liquor containing 490 ppm Ca, 97 ppm Mg, 720 ppm Fe in addition to 20,000 pCi Ra/litre. The mass interference of the Ca + Mg + Fe cation concentrations in the feed liquor was in over powering competition, for resin sites with the Ra cations. To obtain realistic data, the adsorption process should be reexamined using a chloride liquor produced under optimal chloride leaching conditions of an Elliot Lake uranium ore. This would in probability reveal other cations unavailable in the synthetic chloride liquors.

- (35) Gilmore, A.J. "The removal of radioactive radium (Ra-226) from pilot-plant acidic chloride liquors, by batch adsorption, with inorganic and organic adsorbents - Progress report no. 5" CANMET Report ERP/MSL 82-124 (TR) (1982).

The addition of an alkali to increase pH of recycle liquor for mineral adsorption testing would (1) add another cation to compete with the Ra on a mineral adsorbent (2) form precipitates and only produce another radioactive product for necessary disposal and (3) add another reagent cost to the Ra removal program.

The 23 g free HCl/litre (0.63 N HCl) dissolved most of the mineral adsorbents. The best non-soluble mineral adsorbent was fine barite, but then only 40.5% of Ra was removed with a loading of 1170 pCi Ra/g. The Dow Chemical (XF 43230) resin removed 83.6% of Ra at a loading of 2418 pCi Ra/g. The minerals containing ions of  $\text{PO}_4$ , K, Na, Mg, Fe, Al, W,  $\text{NH}_4$ , Ca, Ti, Si, Mn and Sn were soluble in the 0.63 N HCl liquor. HCl, in addition, is a typical desorbing reagent of Ra from cation exchangers.

Barite, as one of the three insolubles, should be Ra loaded to saturation by batch adsorption. Then attempts to desorb the Ra with pH 5.0 water should be undertaken. Possibly some freezing tests, under winter conditions, to observe any changes should be done - followed again with further desorption by a pH 5.0 aqueous mixture. These tests should indicate the stability of the Ra-barite mixture. The barite, from Five Island, N.S., should be procurable at a reasonable cost. We should be on the look-out for other available non-soluble minerals as potential adsorbents.

- (36) Gilmore, A.J. "The removal of sulphate, nitrate and ammonia from mine and mill effluents" CANMET Report EMT 73-16 (1973).

Investigative work to-date, on a tailing dam overflow emanating from a mining property shows that:

- (1) the contaminants, sulphate and nitrate anions, may be readily reduced to  $<9$  ppm  $\text{SO}_4$  and  $<1$  ppm  $\text{NO}_3$  on an anion exchanger.
- (2) at ambient laboratory temperatures, ammonia contamination in tailings may be reduced to  $<1$  ppm by air stripping with about 400 cu ft air/gal at pH 11.0. Reagent costs, for pH adjustment prior to  $\text{NH}_3$  removal, are about \$1.50/1000 gal. Aeration of solutions in storage areas, or the alternative use of Na or Mg-alkali as precipitants in mill circuit, may alleviate the contamination caused by 32 ppm  $\text{NH}_3$  at the tailing dam.
- (3) solutions of NaCl and  $\text{Na}_2\text{CO}_3$  are effective in desorbing  $\text{SO}_4^{2-}$  anion from the exchanger. The chloride solution is the most effective in desorbing both  $\text{SO}_4$  and  $\text{NO}_3$  anions from the exchanger.
- (4) recovery of  $\text{SO}_4$  as  $\text{Na}_2\text{SO}_4$  is chemically feasible from either carbonate or chloride solutions by evaporating and cooling. Recovery from carbonate solutions requires acidification.
- (5) the chemical feasibility of nitrate recovery requires further consideration.
- (6) the replacement of the  $\text{NO}_3$  anion, with the Cl anion, as the agent for desorbing uranium would practically eliminate  $\text{NO}_3$  as a contaminant, as well as facilitate  $\text{SO}_4$  recovery as  $\text{Na}_2\text{SO}_4$ .

- (37) Gilmore, A.J. "The removal of sulphate, nitrate and ammonia from mine and mill effluents" CANMET Report MRP/MSL 75-115 (OP) (1975).

Presented at the Annual Meeting of the Canadian Uranium Producers Metallurgical Committee at CANMET, Ottawa, 15-16 May, 1975.

Investigative work to date, on a tailings dam overflow emanating from a mining property, shows that:

- 1) sulphate and nitrate contaminating anions, may be readily reduced to  $<9$  ppm  $\text{SO}_4^{2-}$  and  $<1$  ppm  $\text{NO}_3^-$  by adsorption on an anion exchanger.
- 2) at ambient temperatures, ammonia concentration in the tailings may be reduced to  $<1$  ppm by air stripping with about 400 cu ft air/gal at pH 11. Reagent costs

for pH adjustment prior to  $\text{NH}_3$  removal, are about 2.50 \$/1000 gal. The aeration of solutions in storage areas, or the alternative use of Na or Mg alkali or hydrogen peroxide as precipitants in mill circuit, may provide a more desirable alternative for reduction of the 32 ppm  $\text{NH}_3$  concentration at the tailings dam.

- 3) solutions of NaCl and  $\text{Na}_2\text{CO}_3$  are effective in desorbing  $\text{SO}_4^{2-}$  anion from the exchanger. The chloride solution is the most effective in desorbing both  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  anions from the exchanger.
- 4) recovery of  $\text{SO}_4^{2-}$  as a non-radioactive  $\text{Na}_2\text{SO}_4$  is chemically feasible from either carbonate or chloride solutions by evaporation and cooling. Recovery from carbonate solutions requires acidification.
- 5) nitrate recovery from desorbing solutions with TBP is technically feasible.
- 6) the replacement of the nitrate anion by the chloride anion as the agent for desorbing uranium would practically eliminate nitrate as a contaminant, as well as facilitate sulphate recovery of the  $\text{Na}_2\text{SO}_4$  salt.

- (38) Gilmore, A.J. "The ion exchange removal of chloride anion from process effluents - A progress report" CANMET Report MRP/MSL 77-1 (1977).

The chloride anion has been removed from a synthetic feed of 2 g Cl/litre using the  $\text{CO}_3$ -form Amberlite IRA-400, to produce an alkaline effluent of <4 ppm Cl. The chloride anion is efficiently desorbed from the resin with carbonate solutions. Increasing desorption temperature from ambient to 36 C reduces desorption volume by about 50%. The recovery of common salt NaCl from the carbonate eluate by acidification of the eluate costs about 2.3 times the current price of the NaCl. The problem becomes one of disposing of product recovery is excessive. Or, possibly, the mixed anion eluate can be utilized in part of the overall process flowsheet. For example, this eluate might be useful as a stripping medium in the solvent extraction circuit.

- (39) Slater, M.J. "Recent industrial scale applications of continuous resin ion exchange systems" CANMET Mineral Processing File 3656 (1980).  
see also J. Sep. Process Technol. 1981, 2(3) 2-12.

A review of industrial applications of continuous ion exchange equipment is presented. In particular recent experience of plants used for water treatment and uranium

extraction is surveyed. It is shown that considerable progress has been made in the last decade. Very large plants are now in successful operation; moving packed beds are generally appropriate for water treatment but fluidized systems are well established for uranium extraction from turbid liquors.

Further progress is expected in the treatment of slurries and in comparison of continuous and multi-fixed bed elution systems.

- (40) Slater, M.J. "Report on the extraction of uranium from the Agnew Lake ore bacterial leach liquor by continuous ion exchange" CANMET Report EMT 72-12 (1972).

The flow rates which could be used in continuous fluidized bed ion exchange are two or three times lower than could be used in fixed bed ion exchange if Amberlite XE 299 resin is employed. Other weak base resins are expected to behave similarly to XE 299.

The strong base resin Amberlite IRA-430 produced better results than the weak base resins.

- (41) Slater, M.J. and Prud'homme, P. "Continuous ion exchange in fluidized beds" CANMET Report TB 158 (1972).

A continuous ion exchange plant using a multi-stage fluidized bed extraction column coupled with moving-bed regeneration and wash columns has been built and tested. Hydrodynamic studies on resins and ore leach pulps have been made and a mathematical model has been developed to predict the performance of the extraction column.

Clarified solutions from the leaching of uranium ore and leach pulps of 5 and 10 w/o have been used with Amberlite IRA-430 ion exchange resin.

The mathematical model requires refinement but its actual performance has been satisfactory for predicting the extraction of uranium.

- (42) Wright Engineers Ltd. "Ion exchange pilot plant" CANMET Contract Report OSQ 78-00151 (1978).

Wright Engineers Limited was retained by Supply and Services Canada to assist CANMET in the design and procurement of a pilot plant for a continuous ion exchange

process. The plant is to recover uranium from mine water at the Beaverlodge mining property of Eldorado Nuclear Ltd. Design engineering was completed January 15, 1979, competitive bids on the equipment were submitted to CANMET on February 16, 1979, and purchase of the equipment was authorized on March 8, 1979. By September 20, 1979, the equipment had been installed in the mine and preliminary testing had been completed. Although some problems arose with the equipment, it is recognized that an object of the pilot program will be to optimize the mechanical and process design, and the Scientific Authority is satisfied that he has a good basis from which to begin from. The final expenditure is estimated to be very close to the contract limitation of \$37,305.75.

- (43) Lucas, B.H. and Prud'homme, P. "Uranium extraction using a deep fluidized bed of ion exchange resin" Hydrometallurgy 8, 123-135 (1982).

A fluidized bed 51 mm diameter, about 2100 mm deep and containing Amberlite IRA-400 resin has been used to extract uranium from sulphate leach liquors. Breakthrough curves were obtained for fixed bed conditions with resin initially in the chloride, sulphate or nitrate form. These curves were analysed to give average diffusion coefficients for extracted species in the resin. The rate data were confirmed by a batch stirred tank experiment, indicating the value of such batch experiments. A continuous counter current experiment was then carried out to demonstrate that laboratory data can be used to estimate the performance of such equipment. Further calculations are required to take axial mixing into account on scaling up the bed diameter.

- (44) Lucas, B.H., Lakshmanan, V.I., Johncox, B.A. and Slater, M.J. "Treatment of Beaverlodge uranium mine water by single stage deep fluidized bed continuous ion exchange" CANMET Report ERP/MSL 81-125 (OP) (1981).

Ion exchange using resins is one of the few processes capable of reducing ionic contaminants in effluents to very low levels. Continuous fluidized bed ion exchange is an advantageous technique for processing dirty effluents and thin slurries. It also reduces resin inventory and equipment cost compared to fixed packed beds. A simple continuous fluidized bed unit has been investigated for treating effluents and its performance is described.

Eldorado Nuclear Ltd. and CANMET have conducted a joint program in which a process was developed for the extraction of uranium from Beaverlodge (Fay) mine water while obtaining design data from a 0.76 m diameter column. This paper describes the bench scale process development and the subsequent pilot plant operation at the mine site.

- (45) Prud'homme, P. and Lucas, B.H. "Construction and operation of a continuous ion exchange pilot plant using fluidized bed columns" CANMET Report 79-9 (1979).

The development of new simplified ion exchange equipment for recovering metals from solution is described. For many years fixed bed ion exchange has been practised on clarified liquors. A more economic treatment was realized by constructing a continuous ion exchange plant in which resin inventory is reduced and solution filtration and clarification stages eliminated. The equipment consists of a single stage deep fluidized bed extraction column coupled with moving bed elution and wash columns for the extraction of different ions from mine water solutions and leach liquors. A procedure was developed to achieve the proper utilization and optimum operating conditions for this pilot plant equipment.

- (46) Lucas, B.H. "Separation processes by single stage deep fluidized bed continuous ion exchange" CANMET Report MRP/MSL 78-150 (OP&J) (1978).  
see also CIM Bulletin 1980, 73(815) 195-200.

The four processes tested on a mini pilot-plant scale have shown that a deep single-stage fluidized bed extraction column for incorporation into a continuous ion exchange system is feasible. Certainly the design of CIX column has been simplified.

The kinetics of the resin are quite important in sizing the equipment and therefore obtaining the desired reduced resin inventory. The kinetics of the A 200 cation resin are much more favourable than the slow IRA 400 resin when considering treatment of waste waters. The low resin loading achieved in these processes results in less selectivity and very low effluent values which, of course could be considered desirable in treating mine waters. The use of plant size columns at an optimum diameter ratio would increase the metal concentration in the eluate over that obtained in the pilot plant, since it was not possible in the mini pilot-plant to obtain the best ratio. The elution column sizing is a matter of maintaining a desired low flowrate. Therefore a small diameter and height can

be used. In the case of base metal mine-water, an initial concentration of all the metals followed by separation is more economical than processing all of the mine water through a series of large columns to separate each metal individually. The other aspect of CIX, i.e., the treatment of unclarified liquors, has been proven to be no problem in this column. However, the treatment of light slurries has not been tested as yet. The only limitation foreseen is the necessity for a rugged dense resin. It will be interesting to try the recently developed Senbrix(C) dense strong base resin on a uranium slurry. A dense resin is also desirable to reduce settling time in the transfer of resins and avoid loss by elutriation.

- (47) Lucas, B.H. and Prud'homme, P. "Progress report on the separation of uranium from leach liquors by single stage deep fluidized bed ion exchange" CANMET Report MRP/MSL 77-53 (TR) (1977).

A single stage deep fluidized bed continuous ion exchange column has been successfully used to co-extract uranium and thorium from  $H_2SO_4$  uranium liquor. Extraction of 99.96% uranium and 95.0% thorium, were achieved. The benefit of this column over fixed bed ion exchange is that unclarified liquor or dilute slurries could be treated thus reducing costs, as well as reducing resin inventory.

It is planned to test and evaluate a conceptual flowsheet for the co-extraction of U and Th by CIX, then to subsequently separate U and Th by solvent extraction to produce high grade products.

- (48) Lakshmanan, V.I. and Sober, D.L. Ontario Research Foundation "Recovery of gold by single stage deep fluidized bed, ion exchange and carbon technique" CANMET Contract Report 1SQ 85-00064 (1986).

Carbon-in-pulp (CIP) processes are now widely applied in the major gold producing countries for the recovery of gold from pregnant leach solutions. The technique provides significant economic benefits over the Merrill-Crowe process. The next generation of gold recovery methods is likely to include continuous fluidized bed type adsorption process and a more economic desorption process. Such a system using ion exchange resins to recover elements such as uranium is well developed in the mineral industry. However, these multi-stage systems have complicated internals and control systems to regulate resin movements. In comparison single stage deep fluidized systems

have the attraction of relatively simple engineering and have been proposed for the recovery of metals from solution.

Prior to the development of such an extraction system it has been found necessary to conduct bench scale evaluations to determine the adsorption and elution characteristics of both ion exchange resins and activated carbon.

The present report summarizes the development work conducted for the project as described in Proposal No. P.4780-G issued to DSS under Contract No. ISQ85-00064. The objective of the program was to evaluate, on the bench scale, the adsorption, elution and electroelution efficiencies of ion exchange resins and activated carbons as applied to gold solutions.

The following elements were involved in the objectives:

- computer assisted literature review of all available related data
- stir tank adsorption tests on activated carbon and ion exchange resins
- column adsorption of ion exchange resins
- stir tank elution of ion exchange resins
- pressurized caustic cyanide elution (Zadra) of activated carbon
- electroelution of activated carbon.

- (49) Lakshmanan, V.I., Biskupski, J. and Eberts, D. Ontario Research Foundation "Recovery of gold by single stage deep fluidized bed, ion exchange and carbon technique" CANMET Contract Report 69054-01-SQ (1987).

Recovery of gold from aqueous gold containing solutions by carbon and ion exchange methods has been carried out. The use of CANMET single stage fluidized bed as a contactor device has been evaluated. Based upon the test results obtained, it is believed that strong base anionic resin can be considered as an adsorbent for unclarified heap leach type solutions obtained from placer type ores using CANMET single stage deep fluidized bed. The presence of dissolved base metal ions significantly reduces gold loading capacity. The use of (i) potassium thiocyanate in di-methyl formamide and water or (ii) electroelution procedures offer alternatives to acid elution methods for recovering gold from loaded resin column.

Economic comparison of gold recovery from heap leach type solutions, without the presence of base metal ions, indicate the use of single stage deep fluidized bed ion exchange column with strong base resins to be higher than conventional activated carbon

route. This is entirely due to the present cost of resin (IRA-400) tested as against carbon cost.

- (50) Lucas, B.H., Ritcey, G.M. and Slater, M.J. "Use of continuous ion exchange for processing waste streams for removal of environmental contaminants" CANMET Report ERP/MSL 75-71 (OP&J) (1975).  
see also CIM Bulletin Aug. 1978, 117-123.

Ion exchange using resins is one of the few processes capable of reducing ionic contaminants in effluents to very low levels. Continuous ion exchange is an advantageous technique for processing dirty effluents and thin slurries. It also reduces resin inventory and equipment cost. A simple continuous fluidized bed unit has been designed for treating effluents and its performance is described.

Breakthrough curves were obtained from fixed fluidized beds which were then used to develop a design procedure for continuous and periodic flow countercurrent fluidized bed ion exchange system. A typical waste stream containing about 60 ppm copper was treated in a continuous system at a flow rate of 900 gph/sq ft, yielding a raffinate containing less than 0.02 ppm copper. The cost for processing such solutions using the proposed fluidized bed system is estimated to be substantially lower than if a conventional fixed bed ion exchange system were used.

- (51) Gilmore, A.J. "A review of some of the resin-in-pulp processes" CANMET Report EMI 67-4 (1967).

In attempts to reduce huge costly liquid solid separation equipment in milling, the ion exchange technique has been modified to recover metal ions directly from a finely ground leach pulp. This modification is called "Resin-in-Pulp" or RIP process. The chemistry of this modification is identical to that of columnar ion exchange. Several pieces of mechanical equipment have been devised that could be useful for the physical contacting of resins with leach pulps to assure adequate metal adsorption. Some of the many processes mentioned in the literature, are adaptations of those reviewed here.

- (52) Ritcey, G.M., Slater, M.J. and Lucas, B.H. "A comparison of the processing and economics of uranium recovery from leach slurries by continuous ion exchange or solvent extraction" CANMET Report EMA 72-26 (OP) (1972).  
Presented at Second Int. Symp. Hydrometallurgy 1973, 419-474.

The recovery of uranium from acid leach slurries by continuous ion exchange, or solvent extraction using sieve plate pulse columns, is compared. Differences in processing costs are of prime concern and can be related to differences in the unit operations of the two methods, as well as to the chemical and physical properties of the slurry. Parameters are defined for the operation of the solvent-in-pulp process and for the design of the continuous ion exchange column. Pilot plant operating experience with both recovery systems is described, and an overall assessment of the relative costs is presented.

- (53) Gilmore, A.J. "A study of the physical stability of some ion exchange resins" CANMET Report IR 69-39 (1969).

In a comparative study the relative physical stability of 14 ion exchange resins was evaluated for potential use in resin-in-pulp processes. When tumbled over a period of time with a 50% pulp of quartz and water a wide range in the physical stability of resins was noted.

The volume loss of the anion exchanger Dowex 21K was only 1.5% after 6 days of tumbling. The cation exchanger Dowex 50W x 8 lost 7% of its volume in 4 days. By comparison several resins had high initial volume losses of from 11 to 20% in the first day. These losses escalated to 28 and 46% after 11 to 20 days.

When a resin-in-pulp process is being considered this study shows the importance of selecting a resin for low attrition losses, as well as for high metal capacity and suitable operating characteristics.

- (54) Gilmore, A.J. "Proposed use for ion exchange in gold cyanidation" Can. Mining J. 1967, 88(5) 63-65.

Studies were made of the feasibility of recovering Au directly from cyanide pulps by a resin-in-pulp technique. Cyanide liquor was placed in contact with Amberlite IRA-400 resins in a series of agitators. Au recovery was >99.9% with Au concentration in

the barren effluent  $< 0.00005$  oz/ton solution Au was desorbed from the resin by an electrolytic process. The  $\text{Au}(\text{CN})_2^-$  anion was first desorbed from the resin to the thiocyanate electrolyte, and then metallic Au was deposited on a Pb cathode. This recovered 98% of the gold from the resin, and the barren electrolyte contained  $< 0.005$  oz Au/ton solution. A pulse column technique was also studied for contact of the resin with the cyanide pulp. This process allows recovery from the agitator.

- (55) Laird, J.L. and Bartlett, D.R. Witteck Development Inc. "Evaluation of resin-in-pulp Technology for Canadian gold ores - Phase II" CANMET Contract Report 69053-01-SQ (1987).

A ten day pilot plant campaign to demonstrate the resin-in-pulp process has been completed. The objectives of the program were to:

- Confirm that the benchscale flowsheet developed during phase I is operative on a pilot scale.
- Confirm the adsorption capacity and selectivity of the chosen resin for gold.
- Confirm that acceptable barren levels (0.01 mg/L gold) can be attained.
- Confirm the resin elution characteristics for gold recovery.
- Evaluate long-term resin poisoning, scaling and attrition by recycling the resin through multiple adsorption/elution cycles.
- Monitor resin handling procedures.

Due to a combination of inconsistent resin characteristics (adsorption capacity and elution performance) and process scale-up problems, not all of the program objectives were achieved. While the gold selectivity of the resin batches did not vary significantly, the gold adsorption capacity of the resin used herein was lower than that tested during the Phase I program. Also, the resin received for the pilot program could not be eluted to the required residual gold level in a reasonable number of eluant bed volumes (e.g. 10 to 15).

Consequently, acceptable barren levels (0.01 mg/L gold) in the treated pulp were not obtained during the pilot operations. However, by utilizing fresh resin rather than eluted resin, and by increasing the resin to pulp flow ratio, a barren level of 0.1 mg/L gold was achieved.

Due to excessive number of eluant bed volumes required for elution, the resin could not be recycled through multiple adsorption/elution cycles. Thus long term resin

poisoning and scaling information could not be obtained. However, the evaluation of resin attrition was completed in an independent study. Resin attrition was found to be negligible compared to carbon attrition under similar operating conditions. Resin handling was not a problem. The plus 32 resin retained efficiently by the 48 mesh interstage screens. All of the resin added to the RIP circuit was recovered within experimental error. In practice, the resin bead and interstage screen sizes would be larger and comparable to those used in CIP operations.

As a result of the resin performance anomalies, a follow-up laboratory test program was designed and completed to support the tentative conclusions drawn from pilot plant results.

Prior to any future pilot testing, the economic merit of the RIP process should be evaluated using, in part, the information obtained during Phase I and II programs. An engineering feasibility study is recommended to examine estimated operating and capital costs for the resin-in-pulp process compared to those for the carbon-in-pulp process which is in common commercial use.